RSIC-374

EFFECT OF ELECTRIC CURRENT ON THE
DIFFUSION OF IONS IN OXIDE LAYERS

by

F. Schein, B. Le Boucher and P. Lacombe

translated from the French by
U.S. Joint Publications Research Service

February 1965

Redstone Scientific Information Center

U S ARMY MISSILE COMMAND
REDSTONE ARSENAL, ALABAMA

AD

RSIC-374

EFFECT OF ELECTRIC CURRENT ON THE DIFFUSION OF IONS IN OXIDE LAYERS

by

F. Schein, B. Le Boucher and P. Lacombe
Corrosion et Anticorrosion, 10, No. 12, 401 -407 (1962)

translated from the French by
U. S. Joint Publications Research Service

February 1965

EFFECT OF ELECTRIC CURRENT ON THE
DIFFUSION OF IONS IN OXIDE LAYERS

Consequences for the Resistance of Metals to Oxidation*

by

F. Schein, B. Le Boucher   P. Lacombe
French Petroleum Institute,   and   School of Mines, Paris
Corrosion Laboratory   Metallurgical Research Center

After showing why this study is important, the authors
describe the experimental technique and summarize the results.

They have noted a change in the law of oxidation be-
yond a certain current density and a certain duration of
electrolysis, and were able to determine the critical condi-
tions of the appearance of this change.

Without being able to interpret these results, the
authors point out that the passage of a current in an oxide
offers a theoretical tool for the study of oxidation processes,
and furnishes a practical means for slowing down the oxida-
tion of metals.

I. INTRODUCTION

It has already been attempted on numerous occasions to find out
what influence an electric field may have on oxidation phenomena at high
temperatures. Thus Uhlig and Brenner [1] have applied a potential

---

* Communication presented to the "European Corrosion Meeting", organized
in the framework of the International Chemical Arts Conference, Paris,
25 April-4 May 1962.

difference between a copper plate and another plate placed opposite to the
first and separated from it by a layer of air. Fields as high as 15,000
V/cm did not bring about any change in the rate of oxidation of copper at
150°C. D. Ciamaru and G.D. Ciamaru [2] have described analagous experiments
relating to the oxidation of zinc at 400°C. No effect was noted. In these
experiments the field is localized in the dielectric, that is in the air,
and not in the oxide which is the conductor. An internal field could be
brought about only by the passage of electric current.

Hence it was interesting to find out what would happen to the
oxidation of a metal when its superficial oxide is traversed by a current.

II. EXPERIMENTAL TECHNIQUE

To this end, we have prepared cylinders made of pure iron, 5 mm in
diameter and 20 mm in length. These cylinders were oxidized at 860°C in
oxygen so as to cover them with an oxide film having a predetermined thick-
ness. At this temperature the film formed consists mainly of FeO [3]. The
metallic sample was cooled quickly and to its surface a coil of platinum
wire a few tenths of a millimeter thick was wound in such a way that the
spacing between the windings of the coil was approximately one mm. By
connecting the spiral N on one hand, and the cylinder M on the other hand,
to a d.c. source, an electric current may be made to pass through the
oxide (Fig. 1). To measure the true oxidation temperature of the sample,
care must be taken to sink the head of the thermocouple in the mass of the
sample, since the passage of the electric current could provoke an ap-
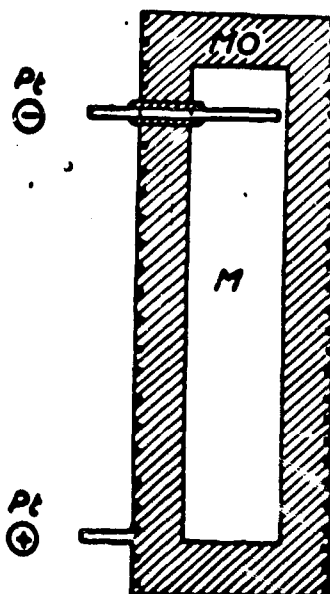preciable increase in its temperature.

Fig. 1. The windings of platinum wire on the already oxidized metallic
sample allow the passage of electric current through the oxide. The
circuit is closed by a platinum wire in contact with the metal but in-
sulated from the oxide layer by means of a refractory cement.

The electric connection between the sample and the source of current requires conductors of sufficiently high diameter. Thus the assembly is much too rigid to allow the taking of measurements by means of a thermo-balance. Hence we have constructed a device in which we measure directly the oxygen fixed by the metal at constant pressure (Fig. 2). The apparatus comprises a silica tube placed in a furnace and connected to a mercury barometer and to a graduated burette which may be filled with the mercury of a reservoir.

After creating a vacuum in the assembly and bringing the furnace to the desired temperature, the pure oxygen is allowed to return to the experimental pressure marked on the barometer. The oxidation begins; when the pressure drops slightly in the barometer, the reservoir is raised so as to replace the volume of fixed oxygen with an equal volume of mercury in the burette. This condition of equality has been attained when the mercury level in the barometer has returned to its initial value. In practice, the sensitivity is greatly increased by measuring the pressure with a butyl phthalate differential barometer; one of its branches is connected to a gas reservoir in which the oxygen is isolated at the initial pressure, the other branch remains in communication with the system.

The device readily permits the detection of the fixing of 0.1 cm^3 of oxygen. However, it obviously requires that the temperature of the device be highly constant. To this end, the entire apparatus (except the furnace) is placed into an enclosure maintained at 30°C $\pm$ 0.1°C. The temperature of the furnace does not vary by more than $\pm$ 1°C in the vicinity of 900°C. The entire apparatus is placed in a room maintained at 25°C $\pm$ 0.5°C. A mechanical device permits raising the mercury level in the burette from a distance, and thus avoids disturbing the temperature of the measurement enclosure during the operation. By raising the mercury a
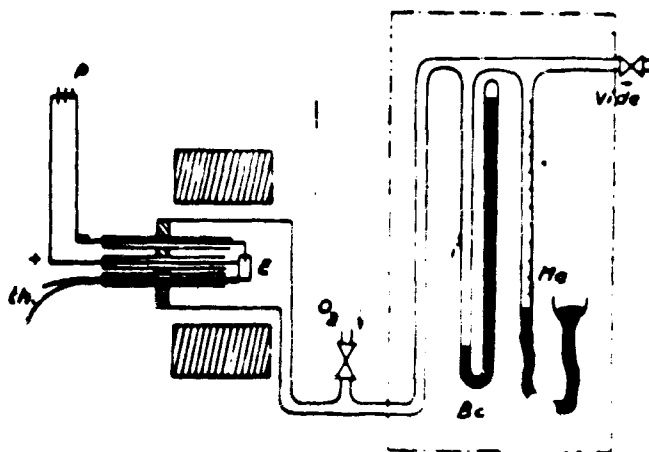

Fig. 2. Volumetric Apparatus for Measuring the Oxidation at Constant Pressure. [vide = Vacuum].

3

little too much, the measurement is reduced simply to recording the mercury level in the burette at the moment when the differential manometer passes through the equilibrium position.

III. RESULTS

Slowing Down of the Oxidation Rate Under
the Effect of a Cathodic Current.

On Fig. 3, we have drawn the oxidation curves of pure iron at 860°C in oxygen under a pressure of 770 mm Hg, at different intensities of current circulating in the oxide. The direction of the current is such that the metal functions as a cathode. It may be seen that, with increasing intensities, the rate of attack of the iron decreases. The logarithmic representation shows that this attack takes place according to a parabolic formula.

If the current is interrupted, the rate of oxidation returns to the usual value as may be seen in the example of Fig. 4 where the current of 3.7 amp/cm^2 was interrupted after three hours of oxidation. After the cessation of current the resumption of the attack may be followed by carrying out an electrolysis of the oxide formed on a tungsten bar. With a
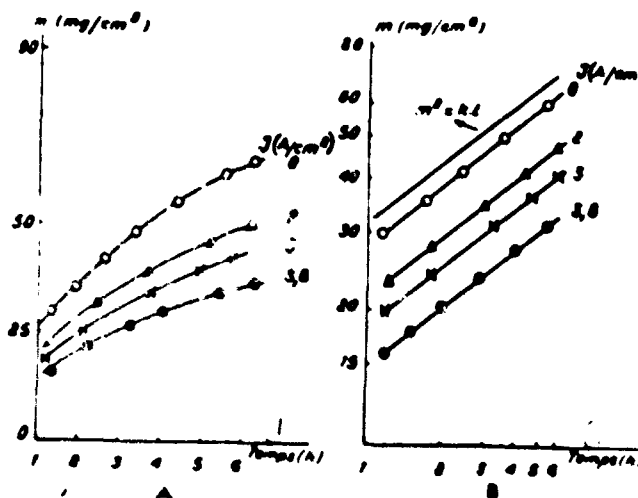

Fig. 3. Slowing Down of the Rate of Oxidation of Iron in Oxygen at 860°C under the Effect of a Constant Cathodic Current. The Effect Increases with Increasing Current Densities.
A) Normal Represer   ; L) Logarithmic Represen_____n, showing that the current applied acts solely on the rate constant, without changing the law of oxidation which remains parabolic.
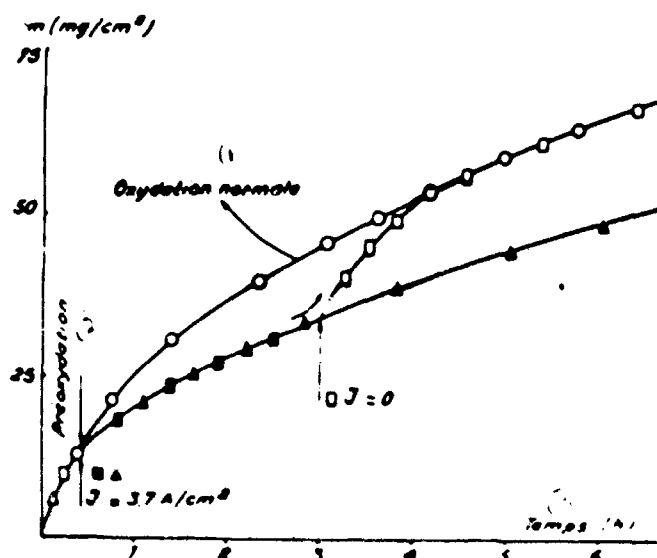1- time, (hr).

Fig. 4. When the Current is Interrupted, the Rate of Oxidation Increases Again, Resuming the Normal Value.
1). normal oxidation; 2) preoxidation; 3) time (hrs.)

4

Fig. 5. Bar of Tungsten Placed in an Oxygen Atmosphere at 1000°C for Three Days, and Subjected to the Effect of an Electric Current Having a Density of 50 m amp/cm^2.
Three hours before withdrawing the sample, the current was stopped in the central part, leading to a strong oxidation of this region.
(Magnification: x 3.5).

cathodic current of 50 m amp/cm^2 the oxidation of the metal at 1000°C is completely stopped. The photograph of Fig. 5 makes it possible to appreciate the sharpness of the phenomenon. The tungsten bar had remained for three days in oxygen at 1000°C crossed by a current having a density of 50 m amp/cm^2. Three hours prior to the stopping of the experiment, the current was stopped in the central part: here the oxidation resumed at a normal rate, that is, very rapidly.

Hence the passage of a current having a direction opposite to that of the natural corrosion current indeed reduces the rate of oxidation of the metal. Conversely, if the metal is made anodic, the rate of oxidation increases [4]. Hence it is possible to act upon the phenomenon of oxidation by the effect of an electric current. But what might be the nature of this effect?

Change in the Law of Oxidation Beyond a
Certain Current Density and a Certain
Duration of Electrolysis.

In order to attempt answering this question, we began by studying the effect of more and more intense currents under the same conditions of oxidation: pure iron at 860°C in pure oxygen. It may be seen on Fig. 6 that, for cathodic densities of 5.6 and 7.2 amp/cm^2, the rate of oxidation is even smaller than before. But, in logarithmic representation, it is found that, for these densities, the parabolic law is no longer followed after a certain time, and that soon a new linear region appears having a smaller slope which may correspond to the appearance of a new oxidation regime.
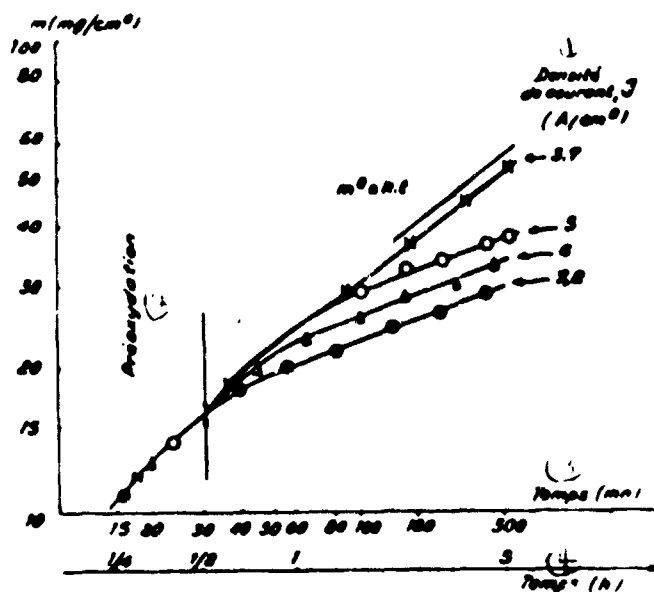
5

Fig. 6. Appearance of a New Oxidation Regime after a Certain Period of Electrolysis whose Length Varies Inversely with the Intensity of the Current. In Logarithmic plotting, the new regime corresponds to the establishment of a new

less steep slope (temperature: 860°C)

1) Current density; 2) preoxidation;
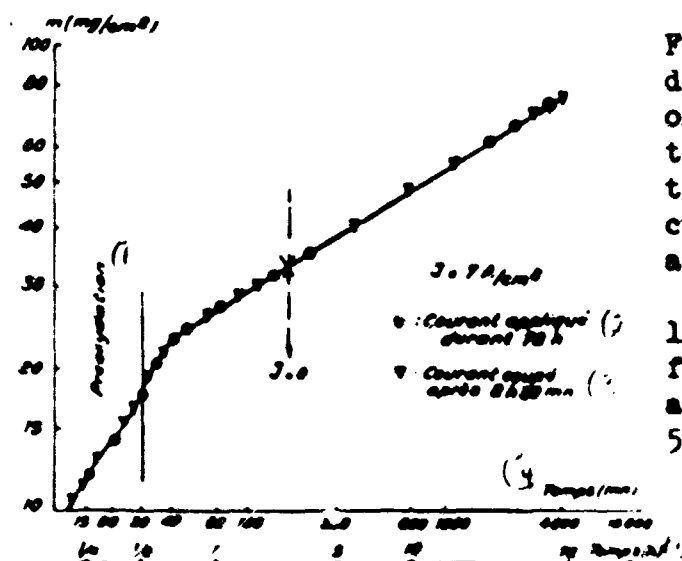3) time (minutes); 4) time (hrs.)

Fig. 7. When we go beyond the conditions of electrolysis which bring on the appearance of the new oxidation regime, the latter persists thereafter even in the absence of current (temperature: 860°C; duration of test 72 hours),

1) preoxidation: 2) current applied for 72 hours; 3) current stopped after 2-1/2 hours; 4) time (min.);
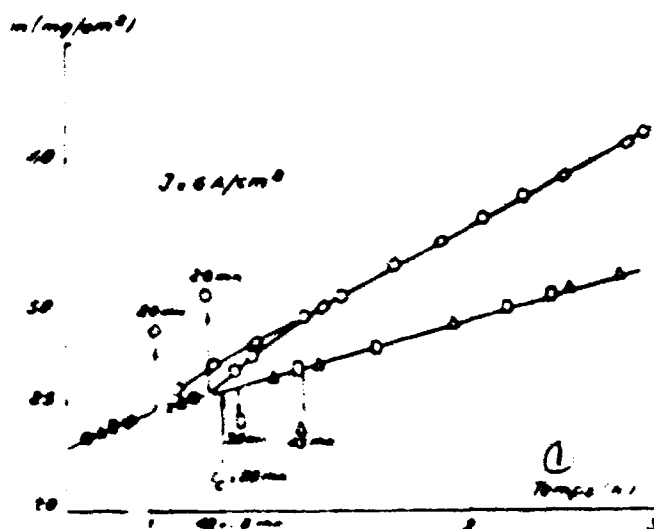5) time (hrs.).

Fig. 8. Determination of the Critical Time of Change of the Oxidation Regime by Examining the Law of Oxidation after the Stopping of the Current after Different - Alternately Very long and Very short - Periods of Electrolysis. The electrolysis starts after 42 minutes of oxidation which served for the forming of the oxide layer subjected to the electrolysis (temperature : 860°C).
(mn = minutes; 1) time (hrs.).

6

If we now stop the current after having entered into the new region, we note that the oxidation does not return to its initial rate as had been the case with smaller densities. It may be seen on Fig. 7 that, after stopping the current, the oxidation continues for long periods of time following exactly the same new law as had been found with the current. The slowing down of oxidation seems to have become permanent. Hence, the electrolysis current, if it is sufficiently intense, leads to a change in the process of oxidation which persists in the absence of the current which has given rise to it.

Now we must find the minimum conditions of electrolysis of the oxide film which cause the appearance of the new law of oxidation and make it persist afterwards even in the absence of current.

Appearance of the Change in the Law of Oxidation
Beyond a Critical Density and a Critical Time

Hence we carry out the electrolysis of the oxide film, formed at $860^{\circ}C$, at a current density of 6 amp/cm^2 for different lengths of time, and we note the behavior of the metal with respect to oxidation after the current has been stopped. The results are plotted in Fig. 8. It may be seen that, after 20 minutes of electrolysis in the presence of oxygen, the oxidation is resumed, following the usual parabolic formula. At the end of 34 minutes, on the contrary, the oxidation phenomenon which has already entered into its new regime stays there: hence the critical time has been exceeded. With a duration of 26 minutes the parabolic formula is still resumed, but after 30 minutes it is no longer met with again. Hence the critical time is between these two values. If we note on the figure that the appearance of the new straight line in logarithmic representation corresponds to a time of 28 minutes, we may consider that the new oxidation regime starts exactly at the critical time. Thus we shall choose 28 minutes as the critical time under these conditions, to wit : $860^{\circ}C$ and 6 amp/cm^2.

NOTE: We have already pointed out that the temperature of the sample is $860^{\circ}C$ by maintaining the furnace at $840^{\circ}C$. In order to realize the oxidation at the desired temperature as soon as the oxygen has returned, it is necessary to heat the sample to $860^{\circ}C$ by a preliminary passage of the current in vacuo, with the furnace at $840^{\circ}C$. How should this period of electrolysis in vacuo be counted in the measurement of th critical time? To answer this question, we have determined this time after varying lengths of time of electrolysis in vacuo. Fig. 9 shows the results obtained at $860^{\circ}C$ with 5 amp/cm^2: the critical time remains 50 minutes, whether the electrolysis in vacuo had lasted 1 hour or 6 hours.

From these facts, two conclusions may be drawn:

1- It is justified to count the critical time from the moment when the oxidation process begins, despite the fact that the current had already circulated under vacuum;
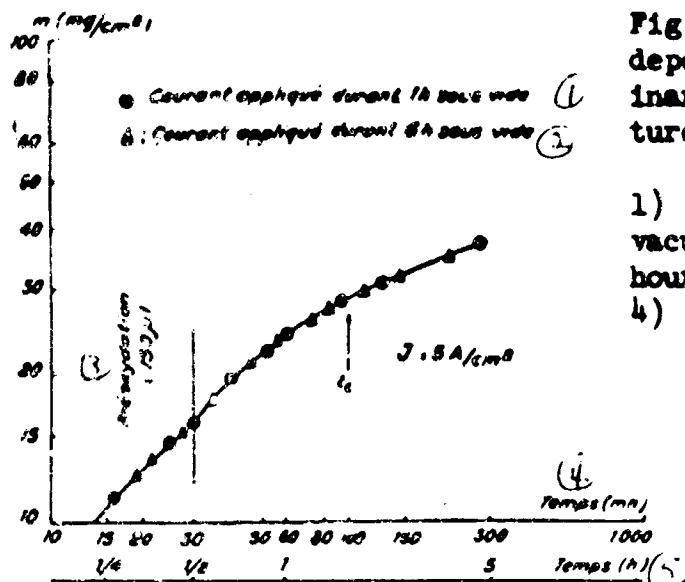
Fig. 9. The Critical Time is Independent of the Duration of Preliminary Electrolysis in Vacuo (temperature : 860°C).

1) Current applied for 1 hour in vacuo; 2) Current applied for 6 hours in vacuo; 3) preoxidation; 4) time (min.); 5) time (hrs.).
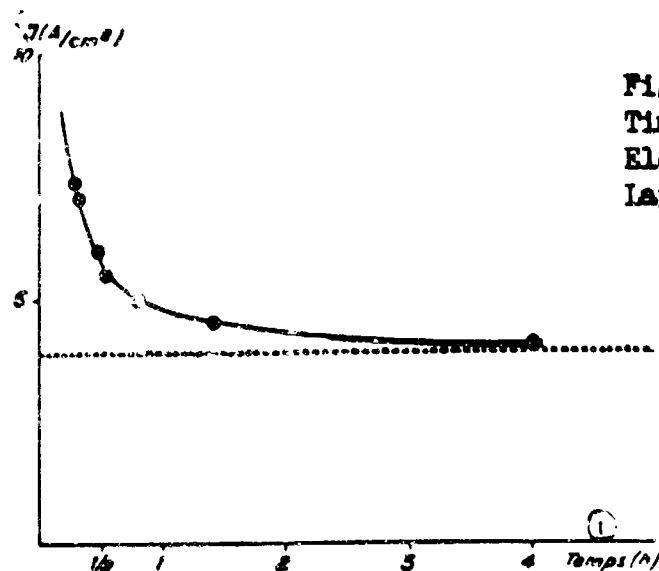

Fig. 10. Variation of the Critical Time with the Density of the Electrolysis Current for an Oxidized Layer 150 μ thick. 1) time (hrs.).

2- Electrolysis of the oxide film in the absence of oxygen does not bring about a change in the subsequent oxidation process.

Then we have measured the critical time for different intensities according to the indicated method with an oxide layer having a pre-electrolysis thickness of 150 μ. The representative curve (Fig. 10) shows that this time increases as the current density decreases. The curve seems to approach a density which will only be attained at infinity. If this were so, it would mean that the new oxidation regime will only be attained at an electrolysis-current density greater than a certain critical value J_o, after supplementary passage of a certain amount of electricity q. If this amount were constant, we would have the relationship:

J (A/cm²)
10

Couche de préoxydation. 150, (1

(2
pente = q

5

J_0
≤ 9

$q = (J - J_0)/t$

$J = J_0 + q/t$

0

$1/t(h^{-1})$

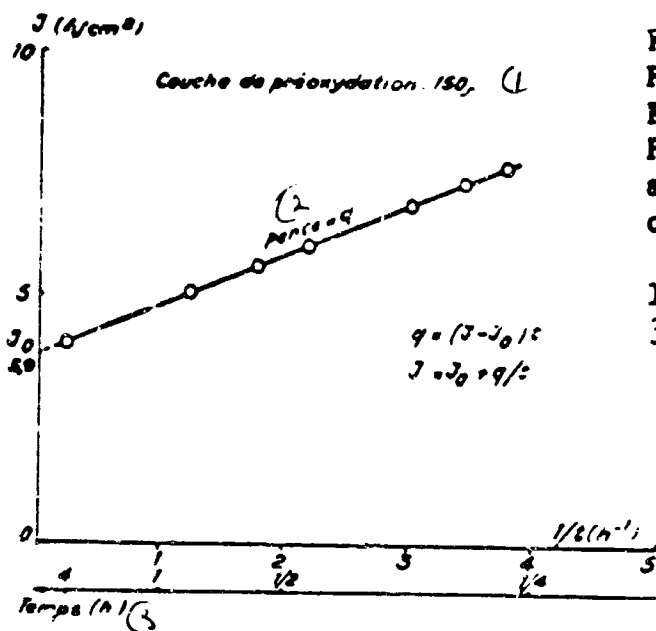4   1   2   3   4   5
      1   1/2   1/4

Temps (h) (3

Fig. 11. Existence of a Linear Relation Between the Density of Electrolysis Current and the Reciprocal of the Critical Time for an Oxidized Layer Having a Thickness of 150 μ (temperature : 860°C).

1) Preoxidation layer; 2) slope;
3) time (hrs.).

$$(J - J_e) t_e = q$$

Such a relationship may be readily verified by putting it into the form:

$$J_e = J + q \times \frac{1}{t_e}$$

By plotting J as a function of $1/t_c$, we see from Fig. 11 that we get a linear relationship. From this the critical intensity I_o, below which it is impossible to obtain the new oxidation regime, is readily obtained by extrapolation. At 860°C, for an oxide thickness of 150 μ , this new regime may be obtained below J_o = 3.9 amp/cm² for an additional amount of electricity of:

$$q = 3\,800 \, C/cm^2$$

On Fig. 12 we have plotted the results relating to an initial oxide thickness of 400 μ; it is seen that the representative points fall on the preceding straight line. This shows that the critical density and time are independent of the oxide thickness.

IV. DISCUSSION OF RESULTS

It is not possible at the present time to interpret these results. However, the following remarks may be made: According to Wagner, whether we consider the phenomenon of oxidation as being linked with the diffusion of ions caused by a concentration gradient, or whether we look upon it as an electric transport of ions under the effect of an oxidation e.m.f., we
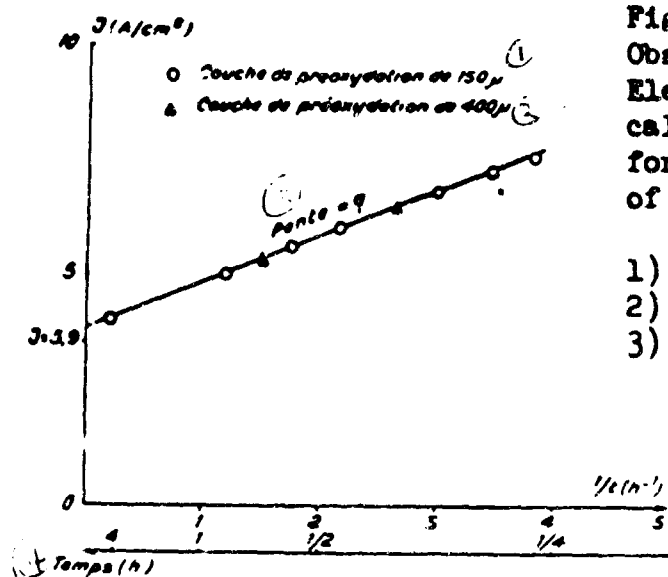
9

Fig. 12. The Linear Relationship Observed Between the Density of the Electrolysis Current and the Reciprocal of the Critical Time is Identical for Oxide Layers Having a Thickness of 150 or 400 μ, (temperature: 860°C).

1) Preoxidation layer 150 μ thick;
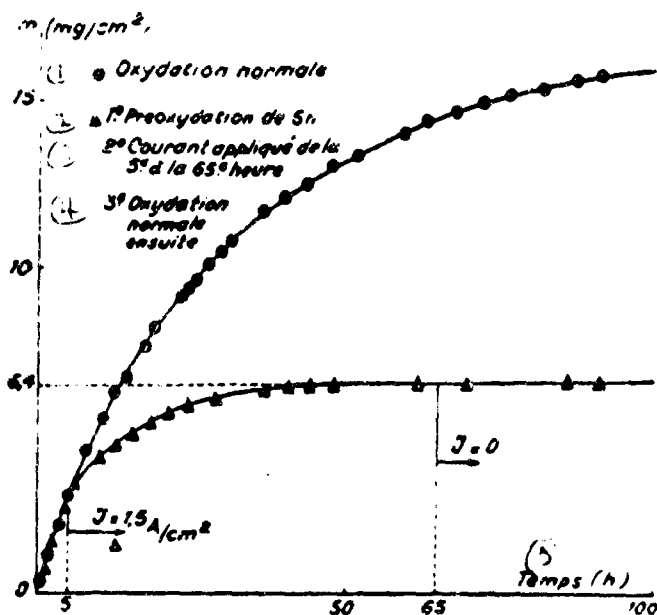2) Preoxidation layer 400 μ thick;
3) slope; 4) time (hrs.).

Fig. 13. Application of a Cathodic Current Through the Oxide Formed on a Steel Sample Containing 18% Chromium, Subjected to the Effect of Oxygen at 950°C, Ends by Totally Stopping the Oxidation, and the Effect persists After the Stopping of the current (duration of tests: 100 hrs.).

1) Normal oxidation; 2) 1. Preoxidation for 5 hours; 3) 2. Current applied from the 5th to 65th hour; 4) 3. Normal oxidation thereafter; 5) time (hrs.)

10

are expressing the same reality. Then if we think that the natural corrosion current is the cause of concentration gradients of cations and anions in the oxide, we see that the current flowing in the opposite direction should reduce them and thus reduce the rate of oxidation. The critical conditions of current density and quantity of electricity would then have, for effect, the reduction of these gradients to zero. Now, parameter measurements, carried out by Demarescaux * on FeO layers having undergone electrolysis at 860°C past the critical conditions, show that the parameter of the crystal lattice seems to be constant over the entire thickness of the oxide.

Hence the artificial current would indeed reduce the concentration gradient in the voids in FeO. But why does the rate of corrosion not become zero; why does it only slow down with the change in kinetics? In addition, it should be noted that with other metals or alloys, the oxidation is completely stopped. Thus with 18% chromium steel (Fig. 13) a current having a density of 1.5 amp/cm^2 stops oxidation at 950°C, and the stoppage persists after the cessation of the current.

Other points also remain unexplained. Why does the electrolysis in vacuo play no part? How does the particular state of the oxide, brought about by means of current, maintain itself after the current is stopped? At the present time we cannot answer all these questions. However these studies show that the passage of a current in an oxide offers a theoretical tool for studying the oxidation processes, by profoundly affecting this phenomenon, and also furnished a practical means for slowing down the oxidation of metals and alloys.

BIBLIOGRAPHY

1.   Uhlig, H.H., and Brenner, A.E., Acta metallurgica, 1955, 3, 108

2.   Cismaru, D., and Cismaru, G.D., First International Congress on Metallic Corrosion, London, April 1961, 194.

3.   Benard, J., and Coquelle, O., C.R. Acad. Sci., 1946, 222, 796.

4.   Schein, F., Boucher, B., and Lacombe, P., C. R. Acad. Sci., 1961, 252, 4157.

---

* At the Metallurgical Research Center, Paris, School of Mines